

Photoaddition of 2,3-Dimethylbut-2-ene to the Benzene Ring. Effects of a Proton Donor

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Summary The photoadditions of 2,3-dimethylbut-2-ene to benzene and hexafluorobenzene proceed mainly by 1,4-'ene-type' addition, which is promoted by a proton donor, and substitutive addition respectively, in contrast with the behaviour of other mono-olefins.

THE photoaddition of unconjugated olefins to benzene to yield 1,3-cycloadducts is well known.¹⁻³ In the case of 2,3-dimethylbut-2-ene, Wilzbach and Kaplan obtained a 1,3-adduct as a minor photoproduct, but did not identify the major adduct.¹ We now report the identification of this major photoproduct, and the observation that its formation is non-stereospecific and subject to catalysis by a proton-donor.

Irradiation (*ca.* 6 W at 254 nm for 6 h) of 2,3-dimethylbut-2-ene in benzene (10% v/v) at 24 °C under nitrogen yields three 1:1 adducts in the ratio 8:4:1. The minor 1,2-adduct (I) was obtained as its Diels-Alder adduct (m.p. 192–193°) with maleic anhydride.† The adduct of intermediate abundance was the known 1,3-adduct (II),¹ while the major product (n_D^{20} 1.4930) is assigned structure (III) (see later) and can be considered as derived from a 1,4-'ene-type' addition of the olefin.

Adduct (III) showed a parent ion at m/e 162 in the mass spectrum, and there were significant peaks at 160 ($-H_2$), 83

($Me_3C^+CMe:CH_2$), and 79 (base peak of cyclohexadienyl ion). The i.r. spectrum showed absorptions at 3100 ($:CH_2$), 3040 ($\cdot CH:CH$), 1640 (C:C stretch), 910 ($:CH_2$, CH deformation), and 700 cm^{-1} ($CH:CH$, CH out of plane deformation), and the u.v. spectrum (n-hexane) had λ_{max} at 217 nm. Complete identification was provided by the 100 MHz n.m.r. spectrum (CCl_4), τ 4.38 [4H, AB q, J 11 Hz, CH:CH; further split (J 1.5 Hz) by the allylic protons], 5.30 [2H, AB q, J 1.5 Hz, $:CH_2$; further split ($J_{cis\ H, Me}$ 0.8 and $J_{trans\ H, Me}$ 1.5 Hz) by the allylic methyl protons], 7.22 [1H, t, J 8 Hz (long-range coupling with the allylic methylene protons), CH·CH:], 7.45 (2H, d, J 8 Hz, $CH_2\cdot CH$), 8.26 (3H, m, $CMe:CH_2$), and 9.02 (6H, s, CMe_2). Both the cyclic allylic protons are further split (J *ca.* 1.5 Hz) by coupling with the cyclic vinyl protons.

At first sight, the formation of adduct (III) might seem likely to involve a *cis*-addition, as in (IV). Surprisingly, the addition has proved to be non-stereospecific, the *cis*:*trans* ratio [*i.e.* (V):(VI)] being concentration dependent. Thus thermal *cis*-1,4-dehydrogenation of the adduct formed from 2,3-dimethylbut-2-ene in hexadeuteriobenzene (10% v/v) led to the loss of D_2 and HD in the ratio 2:7, whereas the corresponding ratio from the adduct formed from a 1% v/v solution was 1:1.‡ The differences in these ratios are consistent with a greater contribution from

† Drs. Wilzbach and Kaplan have kindly communicated to us a report that irradiation of 5–10% solutions of benzene in certain olefins rapidly leads to low stationary concentrations of the 1,2-adducts. We have also observed that formation of 1,2-adducts is favoured by high concentrations of the olefin.

intramolecular hydrogen atom- or proton-transfer at the higher dilution within an intermediate diradical, exciplex, or zwitterion. Addition of the olefin to the benzene ring evidently occurs prior to any hydrogen-atom transfer, since no products derived from $C_6H_7\cdot$ and $C_6H_5\cdot$ radicals (e.g. cyclohexa-1,4-diene, 1,1',4,4'-tetrahydrobiphenyl, biphenyl) were detected, nor was any dehydromer of the olefin found.

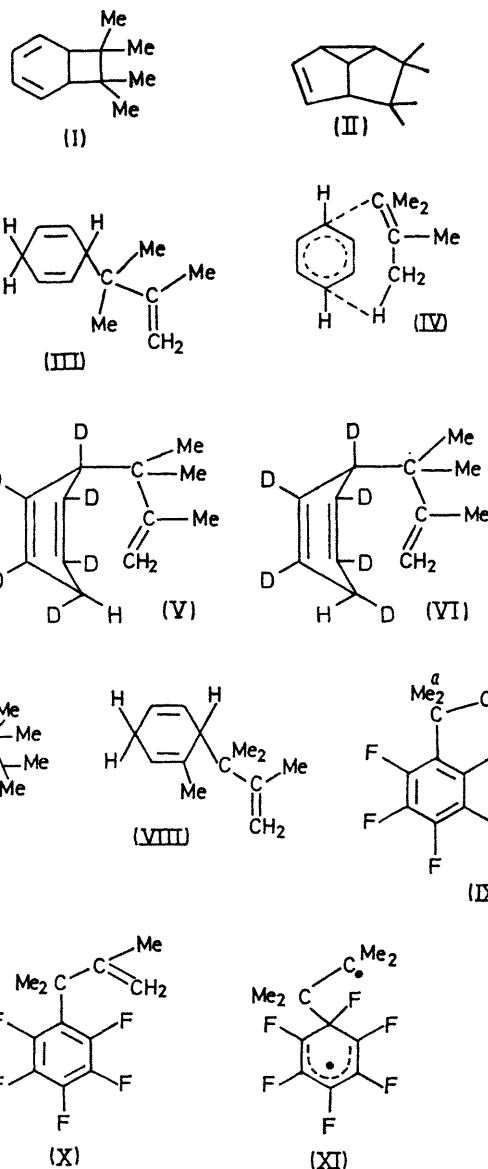
The question now arises whether hydrogen is transferred to the 4-position as an atom or as a proton. Irradiation of the olefin as a 10% solution in benzene-methanol (50% v/v) increased the rate of formation of the adduct (III) by a factor of 2.5, but had little effect on the formation of the 1,3-adduct (II). The use of MeOD led to incorporation of D at the 4-position; no deuterium was incorporated in the dark or on irradiation of adduct (III) in MeOD. This result clearly indicates that proton-transfer promotes the formation of adduct (III) but not of adduct (II). This is the first example of acid-catalysis in a photoreaction between two hydrocarbons. Proton-transfer to the benzene ring evidently follows olefin addition, since irradiation of MeOD in C_6H_6 led to no detectable incorporation of D in the benzene. These results indicate (a) addition of the olefin to excited benzene to give a polarised intermediate, of which (VII) depicts an extreme structure, and (b) concurrent inter- and intra-molecular proton transfer to the carbanion moiety of (VII). Polarity differences do not appear to be important since acetonitrile as solvent had little effect on the rate of adduct formation. In contrast, the H-atom donor ethane-1,2-dithiol inhibited the formation of adducts (II) and (III). This result is being further studied, but is consistent with efficient interception of S_1 benzene by the thiol.

Comparable irradiation of 2,3-dimethylbut-2-ene in toluene (10%) gave four 1:1 adducts; the major one was isolated by preparative g.l.c. and had spectroscopic properties wholly consistent with structure (VIII).

$1 \text{ mol}^{-1} \text{ cm}^{-1}$). The ^1H and ^{19}F n.m.r. spectra (CCl_4) are summarised in the Table.

The minor splittings on the septet fluorine and on the methyl groups (a) may be accounted for by coupling with the *ortho*-fluorine atoms.

The adduct (IX) readily eliminates HF on warming to yield a compound having spectroscopic properties wholly consistent with structure (X). The formation of adduct (IX) is affected neither by the presence of methanol nor of traces of trifluoroacetic acid, and its formation *via* rearrangement of diradical (XI) appears an attractive possibility.



TABLE

	Multiplicity	Splitting, J/Hz	Assignment
$^1\text{H}^a$	t	(6H) 3.5	(a)
	d	(6H) 22	(b)
$^{19}\text{F}^b$	t^c	(2F) Minor couplings, ca. 3.5	<i>ortho</i>
	sept ^d	(1F) 22, ca. 3.5	side-chain
	tt	(1F) 20, ca. 3.5	<i>para</i>
	m	(2F) Major triplet coupling 20	<i>meta</i>

^a In τ .

^b Shifts relative to internal CFCl_3 , $\delta/\text{p.p.m.}$

^c Broad ragged triplet.

^d With minor coupling.

Irradiation of hexafluorobenzene with cyclo-octene gives several 1:1 cycloadducts,⁴ but in contrast, no cycloaddition products were detected with 2,3-dimethylbut-2-ene as the olefin. The major product has been assigned structure (IX), M , 270 (mass spectrum), λ_{max} (EtOH) 262 nm ($\epsilon \approx 600$

† Thermal dehydrogenation of adduct (III) at 350° yields several other compounds in addition to the aromatic product, but the product ratio is the same for the C_6H_6 and C_6D_6 adducts. This absence of a deuterium isotope effect suggests that the D_2 :HD ratios provide a reasonable measure of the *cis*:*trans* ratio in the adducts.

¹ K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1966, **88**, 2066.

² D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.*, 1966, 512.

³ D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47.

⁴ D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.*, 1969, 800.

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